

The calculation of quantum defects in an isoelectronic series based on polarization concepts

By HOWARD A. ROBINSON

It is often of importance, when analyzing a spectrum, to be able to predict a given quantum defect in order to obtain at least approximate absolute term values. The classical method for obtaining such absolute values is of course to fit terms of running total quantum number n to a Rydberg or a Ritz series. Very often, however, a sufficient number of such terms cannot be found and particularly in cases where large values of n and high stages of ionization are involved, experimental accuracy of wave length measurement may not be high enough to give particularly accurate term values. It would, therefore, be convenient to have methods for extrapolating effective quantum numbers along an isoelectronic sequence. A method for accomplishing this in the case of non-penetrating orbits is given in this paper.

In order to make as much use as possible of methods which require the least amount of computation one naturally looks for means by which the least number of significant figures may be used to get the highest degree of accuracy. Thus one is tempted to consider first not the absolute term values themselves but rather the deviation of the absolute values from the corresponding hydrogenic values. Thus if $T_H = -\frac{Rz^2}{n^2}$ represents a hydrogen like term

$$T = -\frac{Rz^2}{n^2} = -\frac{R[z + (\kappa - \sigma)]^2}{n^2}$$

will represent a non hydrogen like term if $z - 1 =$ the stage of ionization, $Z = z + \kappa =$ the atomic number and $\sigma =$ the screening constant. One can then write

$$T - T_H = -2(\kappa - \sigma)\frac{Rz}{n^2} - (\kappa - \sigma)^2\frac{R}{n^2} = Az + B$$

where

$$A = -2(\kappa - \sigma)\frac{R}{n^2}, \quad B = -(\kappa - \sigma)^2\frac{R}{n^2}.$$

Now unfortunately B and A are not true constants in most isoelectronic sequences and thus $T - T_H$ is not strictly linear. This relation thus does not

lend itself too readily to extrapolation use inasmuch as it is actually as simple to estimate changes in n^* with z as it is to estimate changes in σ with z .

A relationship between n^* and σ is easily derived. Since

$$\frac{T}{R} = -\frac{(z + \kappa - \sigma)^2}{n^2} = -\frac{z^2}{n^{*2}}$$

the equation

$$n^* = \frac{nz}{z + (\kappa - \sigma)}$$

follows immediately. It is of interest to examine this relationship for possible minima. In the usual manner it can be shown that n^* will be a minimum when

$$\frac{d(\kappa - \sigma)}{dz} = -\frac{d\sigma}{dz} = \frac{\kappa - \sigma}{z}.$$

It has been known for many years that there are in general two types of curve found when n^* is plotted against z . In the case of penetrating orbits, which are usual with s and p electrons, no minimum is found and the curve increases continuously with z . In the case of non-penetrating orbits, however, the curve goes through a clear minimum. Examples of these two types of behavior are given in Table I and Table II.¹

It is clear that in those cases where one has a minimum $\frac{\Delta(\kappa - \sigma)}{\Delta z}$ is equal to $\frac{\kappa - \sigma}{z}$. Thus the presence of a minimum is caused by the value of σ . This in turn is the justification for the concept of penetrating and non-penetrating orbits.

It is possible by means of another method of attack to obtain extrapolation functions of greater utility particularly in the case of non-penetrating orbits. Previous work² has shown that quantum defects in non-penetrating orbits are largely due to polarization effects. Simple theory developed in the cited references leads to the result that, due to self polarization within the atom, a better approximation to the true term energy is given by

$$\frac{W}{hc} = -\frac{Rz^2}{n^2} - \frac{ae^2}{2hc} \left(\frac{1}{r^4} \right)$$

¹ Data in this paper were taken from the following sources:

The ions of Li through F: From various papers by EDLÉN as given in Atomic Energy Levels, National Bureau of Standards Circular 467, Washington D.C.

The ions of Na, Mg, Al: SÖDERQVIST: Arkiv för Matem. Astr. och Fysik 30 A, No 11 (1944), 32 A, No 19 (1946).

The ions of Si and S: FERNER: Arkiv för Matem. Astr. och Fysik 36 A, No 1 (1948).

The ions of P: Unpublished Data of the Author.

² PAULING: Proc. Roy. Soc. A 114, 181, 1927. — MAYER and MAYER: Phys. Rev. 43, 605, 1933. — VAN VLECK and WHITELAW: Phys. Rev. 44, 551, 1933. — PAULING and GOUDSMIT: The Structure of Line Spectra, McGraw-Hill Book Co. N.Y. 1930.

Table I

O I isoelectronic sequence $2p^3P_2$ (penetrating orbit).

Ion	n^*	$(\kappa - \sigma)$	$\frac{\Delta(\kappa - \sigma)}{\Delta z}$	σ	$\frac{\kappa - \sigma}{z}$
O I	1.0005	0.9990		6.0010	0.9990
F II	1.2471	1.2074	0.2084	5.7926	.6037
Ne III	(1.390)	(1.3166)	(.1092)	(5.6834)	.4389
Na IV	1.4837	1.3920	(.0754)	5.6080	.3480
Mg V	1.5517	1.4446	.0526	5.5554	.2889
Al VI	1.6036	1.4832	.0386	5.5168	.2472
Si VII	1.6446	1.5127	.0295	5.4873	.2161
P VIII	1.6774	1.5386	.0159	5.4614	.1923
S IX	1.7051	1.5809	.0423*	5.4191	.1757

* The increase here is possibly due to experimental inaccuracy.

Table II

C I isoelectronic sequence $3d^3D_3$ (non-penetrating orbit).

Ion	n^*	$(\kappa - \sigma)$	$\frac{\Delta(\kappa - \sigma)}{\Delta z}$	σ	$\frac{\kappa - \sigma}{z}$
C I	2.9556	0.01502		4.98498	0.01502
N II	2.9236	.05246	0.03744	4.94760	.02623
O III	2.9198	.08244	.02998	4.91756	.02748
F IV	2.9191	.11088	.02844	4.88912	.02772
Ne V	(2.925)	.128	(.017)	(4.872)	(.0256)
Na VI	2.930	.14334	(.015)	4.85666	.02839
Mg VII	2.934	.15750	.01416	4.84250	.02250
Al VIII	2.938	.16880	.01130	4.83120	.02110
Si IX	2.942	.17739	.00859	4.82261	.01971
P X	2.944	.19020	.01281*	4.80980	.01902

* The increase here is possibly due to experimental inaccuracy.

where α is the polarizability and $\overline{\left(\frac{1}{r^4}\right)}$, the average value of the reciprocal fourth power of the radius of the electronic orbit, is given by

$$\frac{\frac{3}{2}Z^4 \left[1 - \frac{l(l+1)}{3n^2}\right]}{a_0^4 n^3 (l + \frac{3}{2})(l+1)(l + \frac{1}{2})(l)(l - \frac{1}{2})}.$$

Since for extrapolation purposes one is primarily interested in the energy variation with Z (or z) the question arises as to how α varies with Z . PAULING shows that $\alpha = \frac{K}{(Z - S)^4}$ and remarks that the polarization screening constant S is apparently independent of Z in the Li I isoelectronic sequence. There are, however, other smaller effects which come into play, such as interaction due to some penetration and interaction due to quadrupole effects. Furthermore published values of α show more nearly a variation with $\frac{1}{(Z - S)^3}$. Such effects must also be taken into consideration. One may write

$$\frac{W}{hc} = -\frac{Rz^2}{(n - \Delta)^2} = -\frac{Rz^2}{n^2} - \frac{\alpha e^2}{2hc} \overline{\left(\frac{1}{r^4}\right)}, \quad (n^* = n - \Delta)$$

or, substituting

$$R = \frac{e^2}{2a_0 h c},$$

$$W = -\frac{z^2 e^2}{2a_0 (n - \Delta)^2} = -\frac{z^2 e^2}{2a_0 n^2} - \frac{\alpha e^2}{2} \overline{\left(\frac{1}{r^4}\right)}.$$

Since, assuming $\Delta \ll n$,

$$\frac{1}{(n - \Delta)^2} = \frac{1}{n^2} \left(1 + \frac{2\Delta}{n} + \frac{3\Delta^2}{n^2} + \dots\right)$$

$$\Delta = \frac{n^3 \alpha a_0}{2z^2} \overline{\left(\frac{1}{r^4}\right)} = K' \alpha z^2 + \text{higher terms}$$

where

$$\begin{aligned} K' &= 1.1245 \times 10^{24} \quad \text{for } 2p \text{ electrons} \\ &= .04998 \times 10^{24} \quad \text{for } 3d \text{ electrons.} \end{aligned}$$

It is logical in view of the above mentioned dependence of α on z to try an extrapolation function of the form

$$\Delta = \frac{Kz^2}{f(z)}$$

Table III

Li I isoelectronic sequence. Term $3d^2D_{5/2}$

$$(z + 0.527)^3 + 2.6340z + 0.9413 = 0.10133z^2/\Delta$$

$$\text{Spin orbit correction} = 0.0191z^4$$

z	n^* calc.	Term calc. cm^{-1}	Spin orbit corr. cm^{-1}	Total term calc. cm^{-1}	Term obs. cm^{-1}	(Obs.—calc.) cm^{-1}
Li I	2.998580	12 203.62	0.02	12 203.64	12 203.64	0.00
Be II	2.998186	48 428.22	0.31	48 828.53	48 828.5	0.00
B III	2.998270	109 858.3	1.5	109 859.8	109 859.9	+ 0.1
C IV	2.998445	195 282.0	4.9	195 286.9	195 286.9	0.00
N V	2.998615	305 095.6	11.9	305 107.5	305 105.9	— 1.6
O VI	2.998763	439 296.6	24.8	439 321.4	439 322.7	+ 1.3
F VII	2.998886	597 885.2	45.9	597 931.1	597 934.0	+ 2.9
Ne VIII	2.998990	780 858.4	78.2	780 936.6	—	—
Na IX	2.999077	988 220.2	125.3	988 345.5	988 316*	— 30
Mg X	2.999151	1 219 966	191.0	1 220 157	1 219 930*	—227
Al XI	2.999215	1 476 099	280	1 476 379	1 476 360*	— 19
Si XII	2.999270	1 756 618	396	1 757 014	1 756 930*	— 84
P XIII	2.999318	2 061 524	546	2 062 070	—	—

* These terms were found absolutely by extrapolation of n^* not by calculation of a Ritz series.

Table IV

Li I isoelectronic series. Term $2p^2P_{3/2}$

$$z^4 + 377.681z^3 + 929.960z^2 + 647.511z + 441.808 = 97.513z^2/\Delta$$

$$\text{Spin orbit correction} = 0.091314(z + 0.1)^4.$$

z	n^* calc.	Term calc. cm^{-1}	Spin orbit corr. cm^{-1}	Total term calc. cm^{-1}	Term obs. cm^{-1}	(Obs.—calc.) cm^{-1}
Li I	1.959335	28 582.65	0.13	28 582.78	28 582.76	— 0.02
Be II	1.954080	114 948.4	1.8	114 950.2	114 946.3	— 3.9
B III	1.958273	257 530.1	8.4	257 538.5	257 539.0	+ 0.5
C IV	1.963149	455 562.6	25.8	455 588.4	455 587	— 1.4
N V	1.967393	708 752.0	61.8	708 813.8	708 810	— 3.8
O VI	1.970911	1 016 969	126	1 017 095	1 017 093	— 3
F VII	1 973817	1 380 143	232	1 380 375	1 380 421	+ 46
Ne VIII	1 976235	1 798 230	393	1 798 623	—	—
Na IX	1.978270	2 271 213	626	2 271 839	2 271 832*	— 7
Mg X	1.980001	2 799 070	950	2 800 020	2 798 834*	—186
Al XI	1.981490	3 381 794	1361	3 383 155	3 383 080	— 75
Si XII	1.982781	4 019 379	1957	4 021 336	4 021 170*	—166
P XIII	1.983912	4 711 780	2689	4 714 469	4 714 450*	— 19

* These terms based on extrapolated values of n^* for $3d^2D_{5/2}$; not fixed by Ritz series.

Table V

Calculated and extrapolated values of $2p^2P_{3/2} - 3d^2D_{5/2}$
Li I sequence.

z	ν calc. cm^{-1}	ν obs. cm^{-1}	(Obs.—calc.) cm^{-1}
Li I	16 379.14	16 379.12	— 0.02
Be II	66 121.7	66 117.8	— 3.9
B III	147 679.6	147 678.6	— 1.0
C IV	260 301.5	260 299.6	— 1.9
N V	403 706.2	403 704.7	— 1.5
O VI	577 774	577 769	— 5
F VII	782 444	782 487	+ 43
Ne VIII	—	—	—
Na IX	1 283 493	1 283 516	+ 23
Mg X	1 579 863	1 579 904	+ 41
Al XI	1 906 776	1 906 720	— 56
Si XII	2 264 322	2 264 240	— 82
P XIII	2 652 399	2 652 380	— 19

where $f(z)$ is a polynomial. It turns out that such a function fits remarkably well for the non-penetrating $2p$ and $3d$ orbits in the lithium I sequence. In fitting such functions one must remember that the spin orbit interaction term must first be subtracted from the observed term value. In the two series considered the hydrogenic constants suffice for this purpose. The lower members of the sequence can then be utilized to determine the several constants in the extrapolation function. Results are shown in Tables III and IV. In all calculations in this paper the value of R appropriate to the individual atom has been used.

It should be noticed here that only four significant figures are necessary in the extrapolation for the $3d$ terms and five for the $2p$ terms, due to the fact that the extrapolation is run on Δ . This fact alone makes such methods of extrapolation attractive. A further check with experiment is possible if we compare the calculated and observed values of the $2p^2P_{3/2} - 3d^2D_{5/2}$ transition. The results are given in Table V.

The fact that this method of extrapolation reproduces the minima in the curves of n^* vs. z and at the same time leads to correct values for the $2p^2P_{3/2} - 3d^2D_{5/2}$ transition leads one to believe that some reliance can be placed on it. It is possible to fit power series containing terms in z and $1/z$ to these data. Usually one finds, however, that either the differences, term obs.—term calc., depart more and more from small numbers or else the slope of the curve obtained by plotting

$$2p^2P_{3/2} - 3d^2D_{5/2} - (T_{2p} - T_{3d})$$

against z (where T_{2p} and T_{3d} represent the hydrogenic term values) shows constantly increasing deviations. In fact from the nature of such series one

might expect such deviations to occur for too wide an extrapolation unless the form of the extrapolation formula had an actual theoretical background.

In fitting the two polynomials given in Tables III and IV to the data, the data for the ions through Na IX was considered to be essentially correct and tables of third or fourth differences in z^2/Δ constructed. The higher differences are quite sensitive to small experimental error. By trial one can then construct a final table with the constant third or fourth difference which gives the best fit for the higher members of the sequence. One quickly finds the particular ions which seem to fit the most poorly and hence the ones which presumably contain the greatest experimental errors. In this connection certain of the standard interpolation formulae, such as that due to NEWTON, can be most helpful in determining the final numerical constants.

One can also derive extrapolation functions for penetrating orbits based on the older semiquantum mechanical methods: Δ is, however, much larger than in the non-penetrating case. The result is that one is required to retain so many significant figures in the calculation that the derivation (which leads to quite different extrapolation functions) appears to be of little practical interest.

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